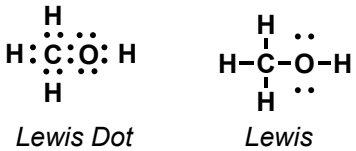
Chemistry 17: Section Handout 1

Topics: *representing organic molecules, Lewis structures, formal charge, resonance structures, isomers, functional groups, the oxidation state formalism*

Key Concept Review

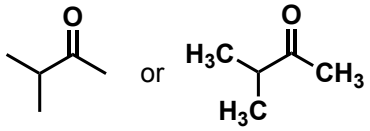
Representing Organic Molecules:

Lewis structures: representations of molecules in which all atoms, bonds, and lone pairs are explicitly shown. Lewis *dot* structures refer specifically to structures in which all bonds are shown as the shared electron dots; Lewis structures refer more generally to structures in which two-electron bonds may be shown as lines.



Lewis Dot Structure *Lewis Structure*

Line/Skeletal structures: "zig-zag" representations of molecules in which carbon atoms are implied at each point and terminus of the zig-zag. Hydrogen atoms bound to carbon and lone pairs are often omitted to save space.



Line/Skeletal Structures

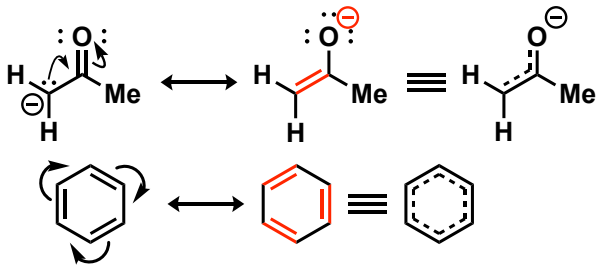
Formal charge: simplified representation of charge distribution in a molecule, considering bonds as completely covalent entities (i.e. assuming that electrons are shared equally between bonded atoms). Formal charges are assigned to each atom in a molecule by comparing the number of electrons assigned to the atom in its molecular state to the number of valence electrons assigned to the atom in its isolated, elemental state.

Formal Charge = (valence electrons in neutral atom) - (unshared electrons) - $^1/_2$ (shared electrons)

Resonance structures: multiple representations of the electronic distribution within a *single molecule*. Resonance structures are used when a single Lewis structure of a molecule is not sufficient to fully describe the delocalization of electrons within a given molecule.

Remember, resonance structures do not depict different molecules; instead, they are multiple depictions of the electron's distribution within the same molecule. The *true* structure is a hybrid of all resonance structures.

The relationship between resonance structures is represented by a two-ended arrow between them. Curved/curly arrows are used to push electrons from a lone pair or bond to a new destination.



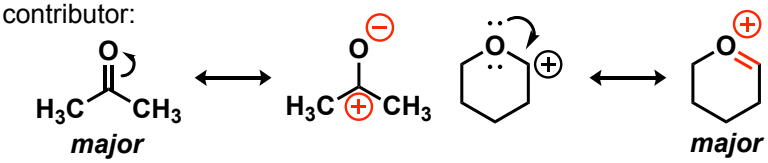
Resonance (Hybrid) Structures:
Each bond is neither a single bond nor a double bond; instead it has a bond order of 1.5.

When drawing a resonance structure, the sigma bonds typically remain in place, while **only** lone pairs and pi electrons (electrons in double or triple bonds) are redistributed.

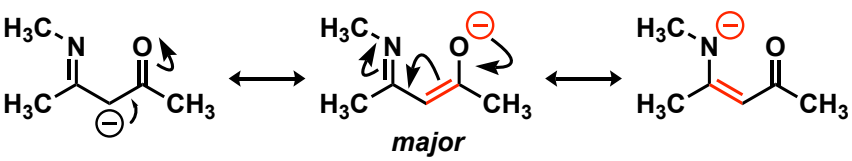
Resonance structures are only considered "important" if they contribute meaningfully to the overall electronic distribution of the molecule. Often molecules will have several "important" resonance structures, but one resonance structure (the "major" structure) most fully describes the electronic distribution of that molecule.

To determine which structure is the major contributor:

(1) look for structures in which every atom has a full octet
(2) minimize charge separation as much as possible (molecules with fewer formal charges are more stable)
(3) if there are charges present, put negative charge on more electronegative atoms and positive charge on less electronegative atoms



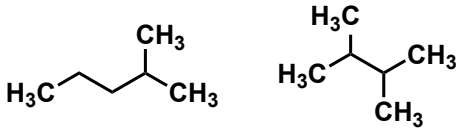
major ***major***



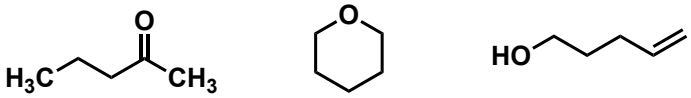
major

Isomers

Structural/Constitutional Isomers: molecules that have the same molecular formula (i.e. are made up of the exact same atoms) but have different connectivity. Since the atoms are connected differently, structural isomers will always be different molecules and do not need to contain the same functional groups.



Structural Isomers

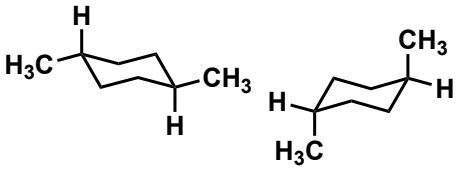


Structural Isomers

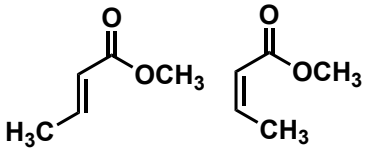
Stereoisomers: molecules that have the same molecular formula and the same connectivity but have different three-dimensional arrangements in space.

Configurational Isomers: stereoisomers that CANNOT be interconverted by rotation about one or more single bond(s). Configurational isomers will always be different molecules but must contain the same functional groups.

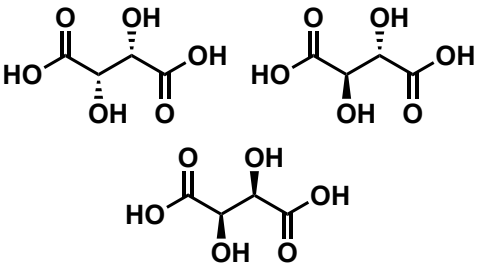
Conformational Isomers: stereoisomers that CAN be interconverted by rotation about one or more single bond(s). Conformational isomers will always be the same molecule, just arranged differently.



Conformational Isomers

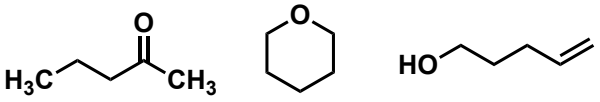


Configurational Isomers

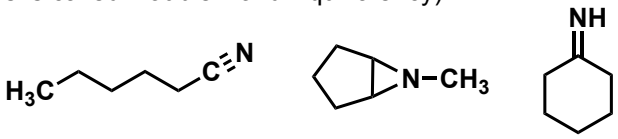


Configurational Isomers

Degree of Unsaturation (DoU): this is defined as the number of pi bonds + the number of rings in a molecule. Isomers must have the same degree of unsaturation, so as to have the same molecular formula. Each ring or pi bond reduces the number of hydrogen atoms in a molecule by 2, as compared to a completely saturated molecule with the same number of carbons and heteroatoms. (In the textbook this is called Double Bond Equivalency).



Structural Isomers with 1 DoU
Formula $C_5H_{10}O$
Formula of completely saturated molecule $C_5H_{12}O$



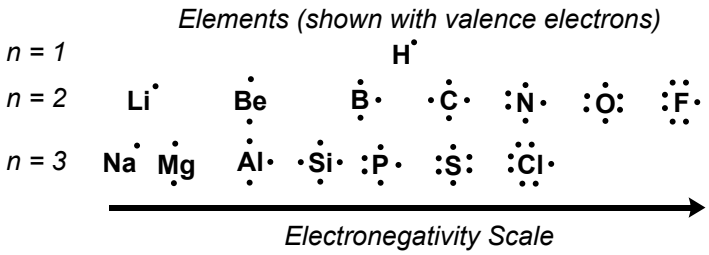
Structural Isomers with 2 DoU
Formula $C_6H_{11}N$
Formula of completely saturated molecule $C_6H_{15}N$

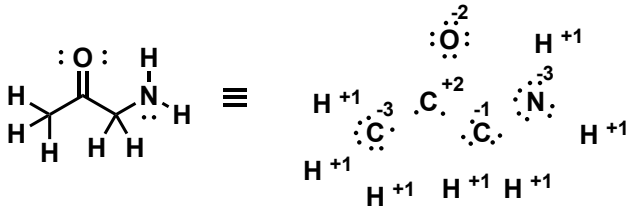
Oxidation State: the hypothetical charge an atom in a molecule would have if all of its bonds were completely ionic. Note that the oxidation state is completely different from the formal charge (which treats all bonds as completely covalent).

To determine oxidation state:

(1) Disconnect all the bonds to the atom in question.
(2) Give all of the electrons from the disconnected bonds to the more electronegative atom in that bond. If two bonded atoms have the same electronegativity, split the electrons in the bond equally between the atoms.
(3) Compare the number of electrons left on the atom to the number of valence electrons that atom has in its isolated, elemental state.

oxidation state =
(# of electrons in elemental state) –
(# of electrons when bonds are disconnected ionically)

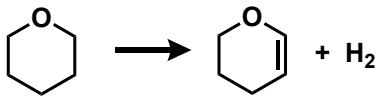




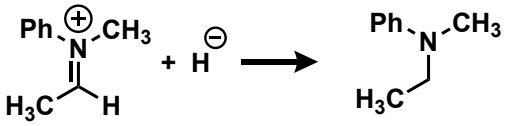
Oxidation: a reaction in which the compound of interest loses electrons. There is a net increase in the oxidation state at the atoms that undergo a change in bonding in the reaction.

Reduction: a reaction in which the compound of interest gains electrons. There is a net decrease in the oxidation state at the atoms that undergo a change in bonding in the reaction.

Redox-Neutral Reaction: a reaction in which the compound of interest neither gains nor loses electrons. There is no net change in the oxidation state at the atoms that undergo a change in bonding in the reaction. Be careful, though: in many redox-neutral reations, the oxidation state may increase for one atom, but decrease for another atom.



Oxidation



Reduction

Redox-Neutral Reaction

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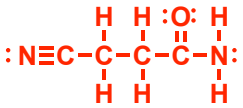
Topics: *representing organic molecules, Lewis structures, formal charge, resonance structures, isomers, functional groups, the oxidation state formalism*

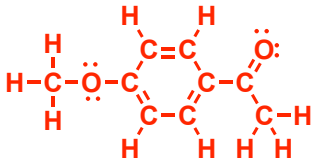
Workshop Problems

1. Provide clearly drawn Lewis structures for each of the following compounds. Use lines for covalent bonds and show all non-bonding electrons (lone pairs). Show all atoms explicitly, even hydrogens**.**

$NCCH_2CH_2CONH_2$

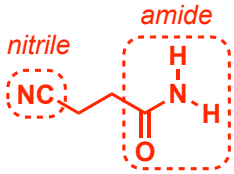


$[4\text{-}(CH_3O)C_6H_4]COCH_3$ **Note:** C_6H_4 is cyclic.

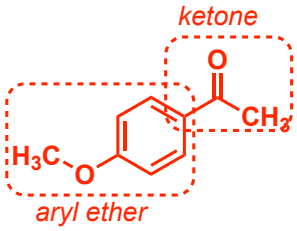


2. Redraw each of the Lewis structures as a line/skeletal structure. Label all functional groups in each compound.

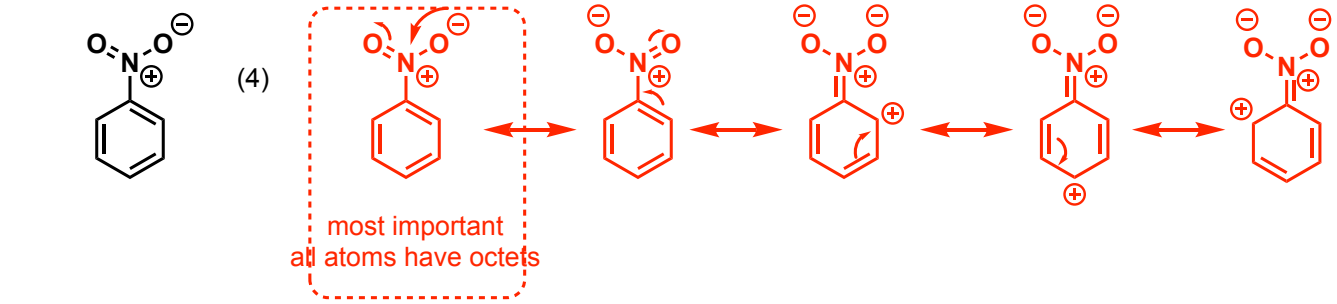
$NCCH_2CH_2CONH_2$

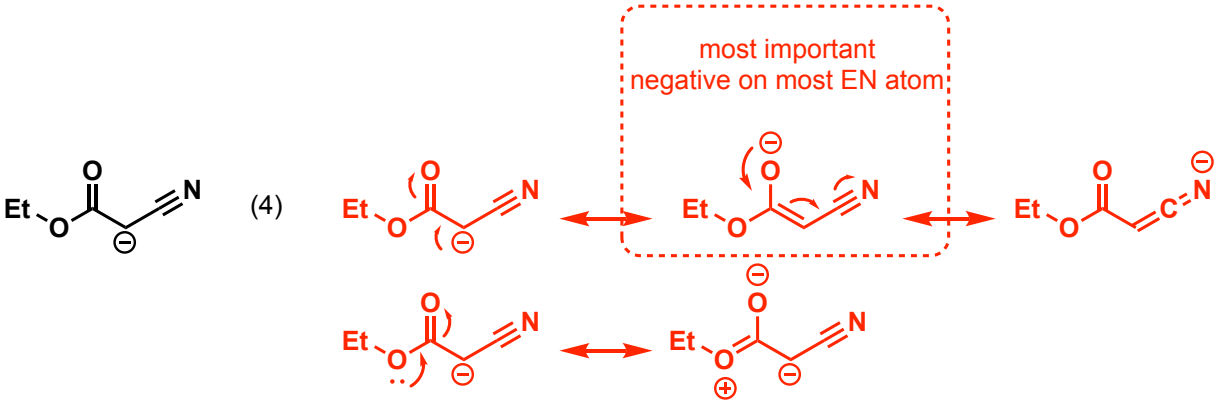


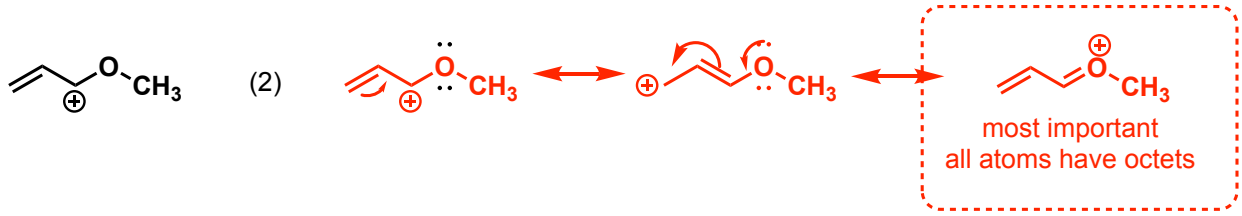
$[4\text{-}(CH_3O)C_6H_4]COCH_3$ **Note:** C_6H_4 is cyclic.



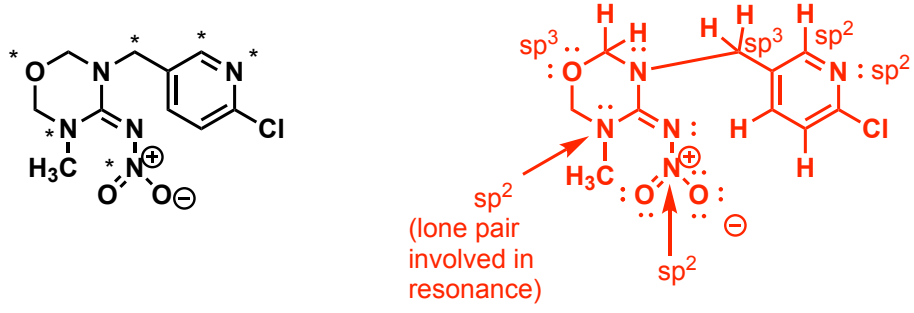
3. For each structure shown below draw the number of **additional** resonance structures indicated. Use the **arrow-pushing formalism** to represent how electron distribution changes between each resonance structure. Draw all lone pairs and indicate formal charges where relevant. Indicate the most important resonance structure(s) in each case giving your reasoning.



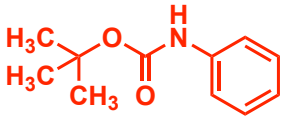




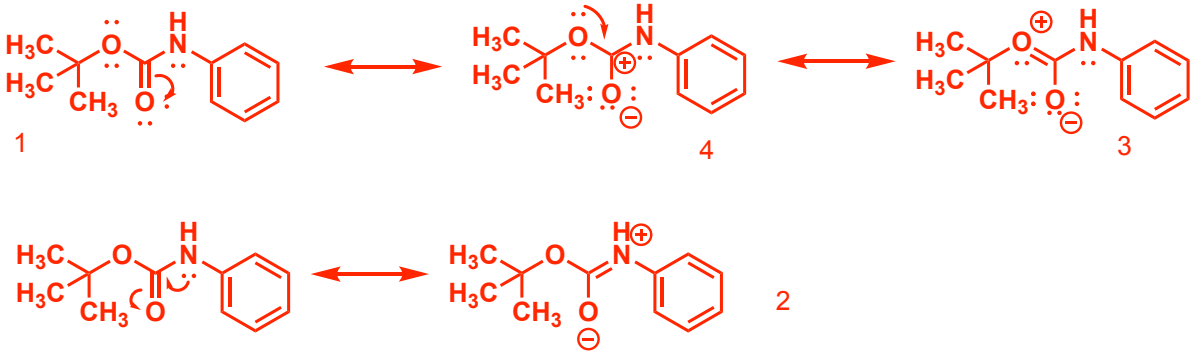
4. The molecule below is a neonicotinoid insecticide, harmful to bees and other insects. Draw in any implied hydrogens, lone pairs and give the hybridization of the marked atoms in the molecule.



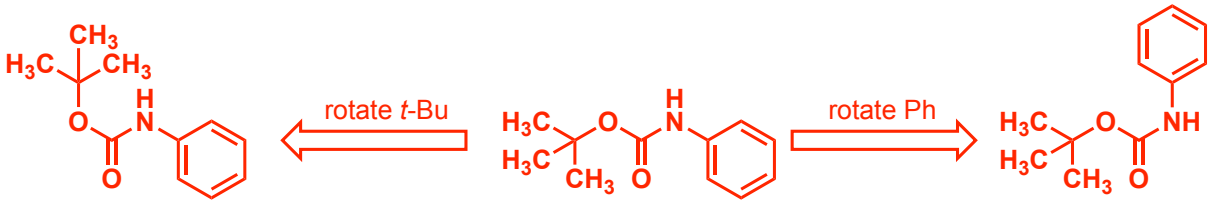
5-a. Draw the skeletal structure of (*t*-Bu)OCONH(Ph).



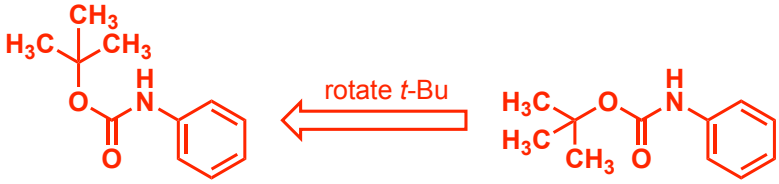
5-b. Draw resonance structures involving the carbonyl group in the molecule only (and not those involving the aromatic ring). Use the **arrow-pushing formalism** to represent how electron distribution changes between each resonance structure. Draw all lone pairs and indicate formal charges where relevant. Rank your structures in order of importance where 1 = most important.



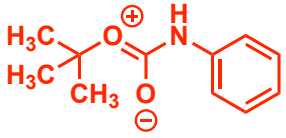
5-c. Conformational isomers of this molecule exist due to rotation around the C-O and C-N bonds. Draw a conformational isomer involving rotation around each bond.



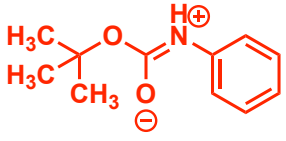
5-d. One of these bond rotations occurs much more easily than the other. Identify which is the easier rotation and explain your reasoning.



The t-Bu conformational isomer exists, but the Ph one does not. This is because the resonance structure involving a double bond between C and N is more important than the one involving a double bond between C and O. Placing a positive charge on N is more favorable than placing a positive charge on O due to the lower electronegativity of N vs O. This is increased double bond character between C and N increasing the barrier to rotation around that bond. The minor resonance structure is not significant enough to prevent rotation of the C-O bond.

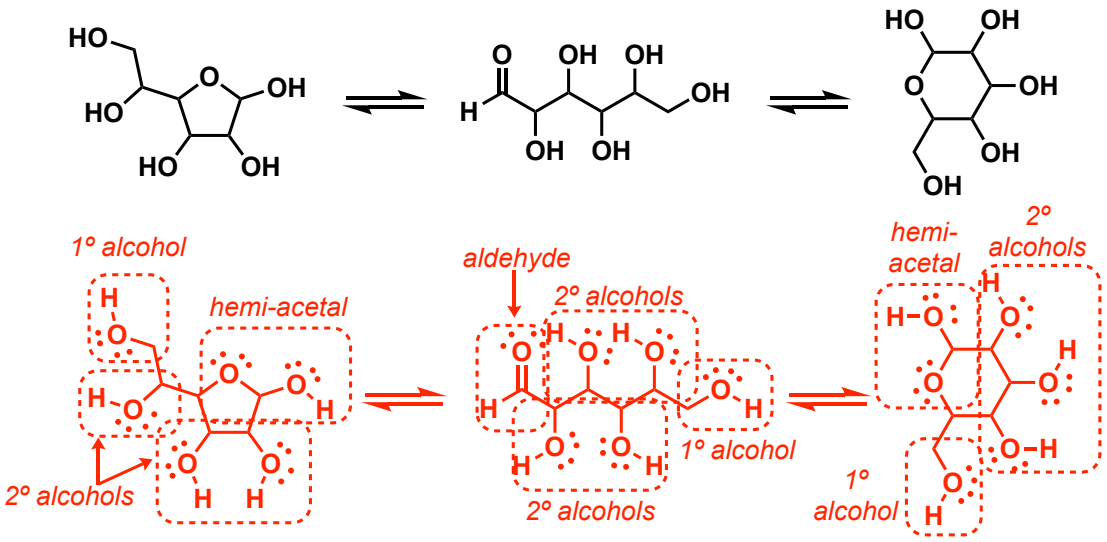


minor resonance structure



major resonance structure

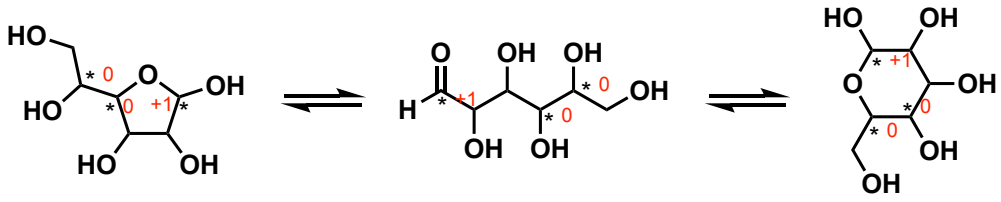
6-a. Identify all the functional groups present in the three molecules below, which are all forms of glucose.



6-b. How are these forms of glucose related to each other? Are they identical molecules? Resonance structures? Isomers? Something else? Justify your answer.

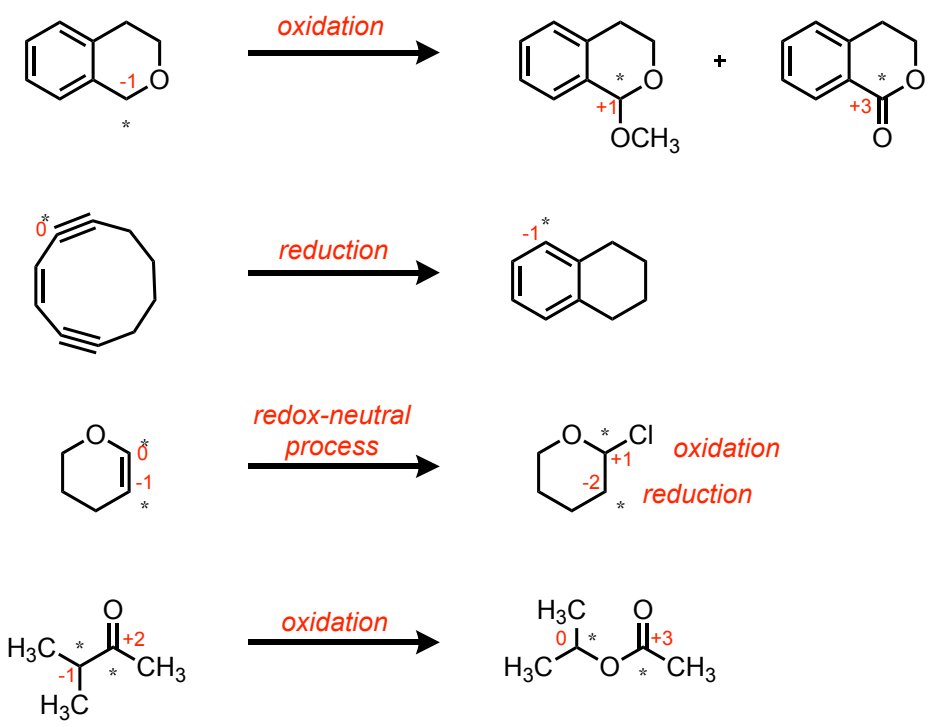
The three forms of glucose are structural isomers of each other. While they have the same molecular formula, their connectivity differs from one to the other (as do their functional groups.)

6-c. Determine the oxidation state at the atoms marked with a star. Is this interconversion between forms of glucose a net oxidation, a net reduction, or a redox-neutral process? Justify your answer.

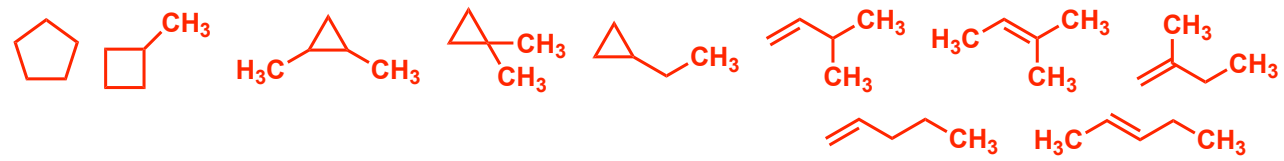


The interconversion between the three forms of glucose is a redox-neutral process. There is no net increase or decrease in the oxidation states at the atoms that undergo a change in bonding in the interconversion.

7. Label the oxidation state of the indicated atoms in the molecules below, and determine whether each transformation is an oxidation, a reduction, or a redox-neutral process relative to the indicated atoms.



8. For the following formula, C_5H_{10}, determine the degree of unsaturation and then draw 10 different structural isomers that would be consistent with that formula.



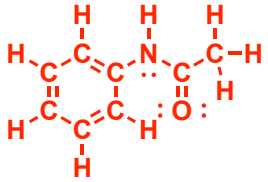
1 degree of unsaturation

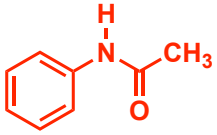
Which of these compounds have a configurational isomer? Draw the configurational isomers clearly using a 3-D representation if necessary to show the difference between then.

Skillbuilder Problem 1: Lewis Dot Structures vs. Skeletal Structures

Provide clearly drawn Lewis and line/skeletal structures for each of the following compounds. Label the functional groups present in each compound, and for the Lewis structures, show all lone-pair electrons.

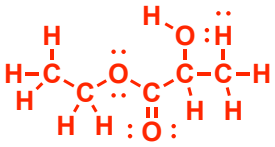
1-a. PhNHCOMe

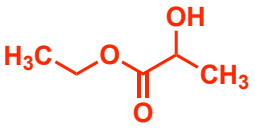




aryl amide

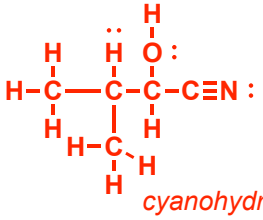
1-b. $EtOCOCHOHCH_3$ (ethyl lactate)



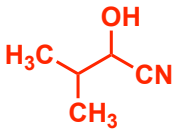


ester, 2º alcohol

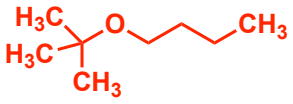
1-c. i-PrCHOHCN

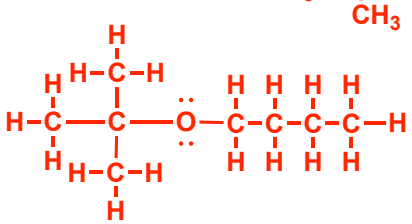


cyanohydrin



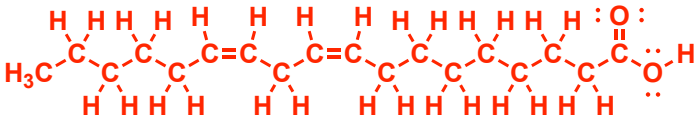
1-d. (*t*-Bu)O(*n*-Bu)





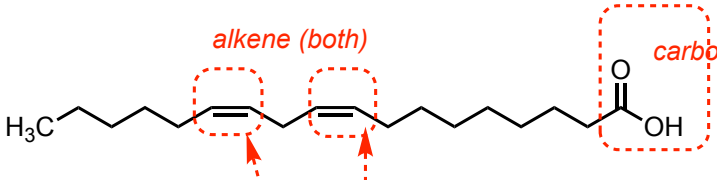
ether

v. $CH_3(CH_2)_4CHCHCH_2CHCH(CH_2)_7CO_2H$



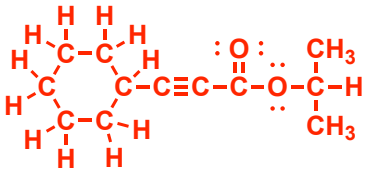
alkene (both)

carboxylic acid



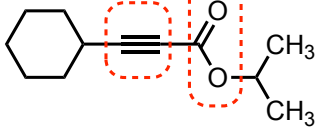
NOTE - there are configurational isomers possible at these double bonds

vi. $(C_6H_{11})CCCO_2CH(CH_3)_2$ Note: C_6H_{11} is cyclic.



alkyne

ester



Skillbuilder Problem 2: Resonance Structures

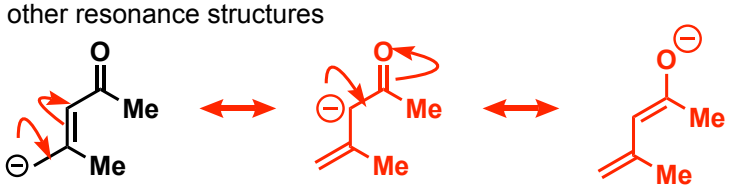
The following compounds can each be depicted using two or more resonance structures. Provide line/skeletal structures of all reasonable resonance forms for each. Use the **arrow-pushing formalism** to represent how the electron distribution changes between each resonance structure. Do not include "no-bond" resonance structures. Indicate formal charges where relevant.

2-a. Hint: shape is linear, 2 resonance structures

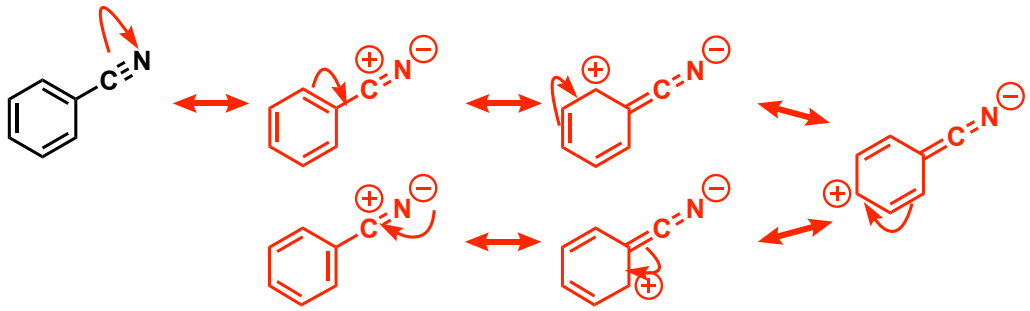
H_3CN_3

2-b. 1 other resonance structure

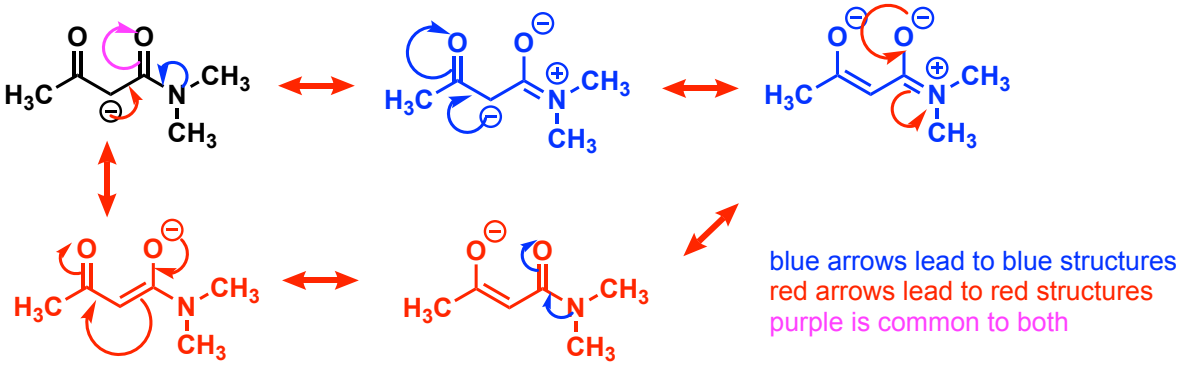
2-c. 2 other resonance structures



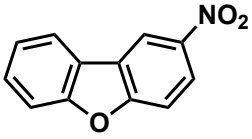
2-d. 6 other resonance structures



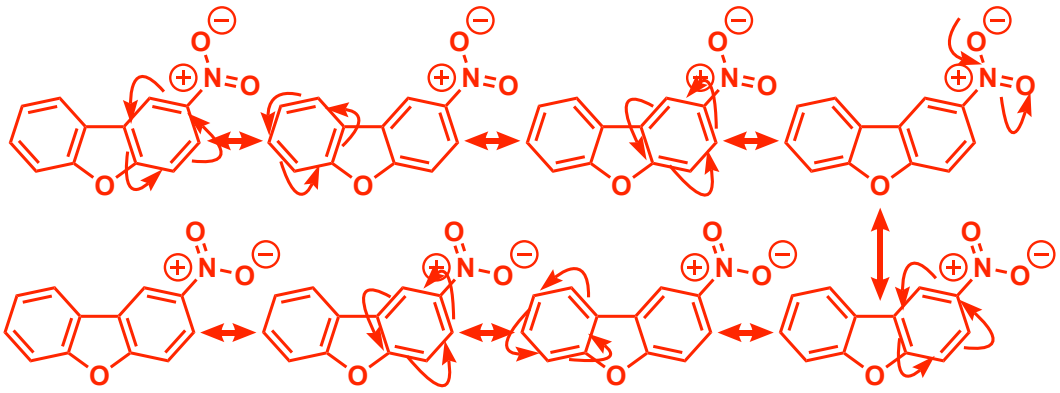
2-e. 4 other resonance structures



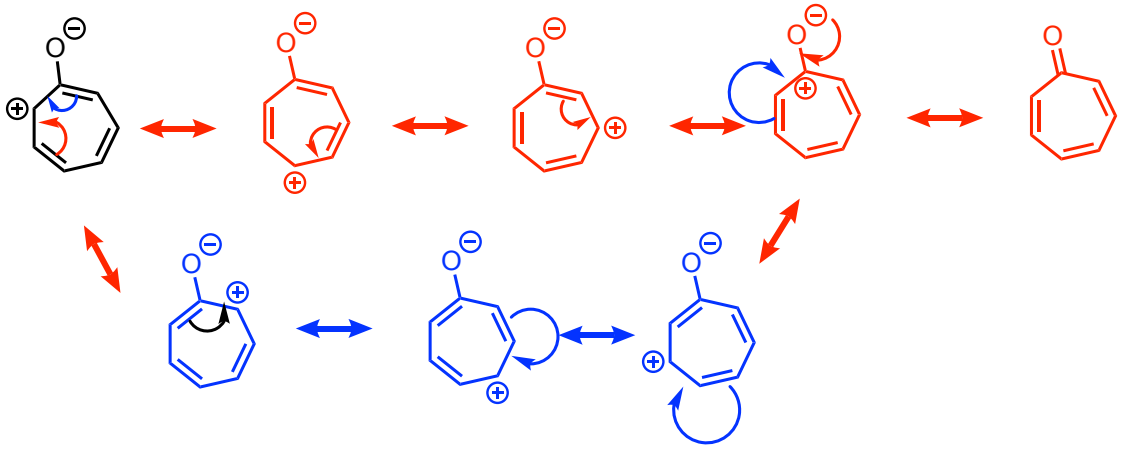
2-f. Draw three most significant contributors only



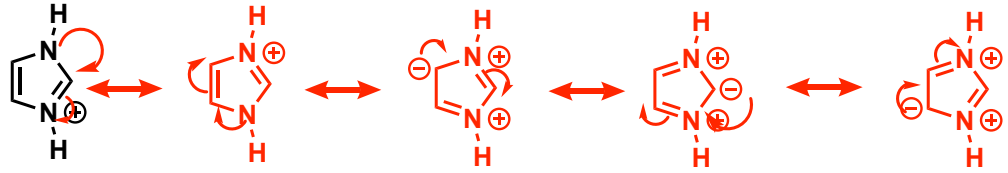
choose any three of the structures shown



2-g. 7 resonance structures



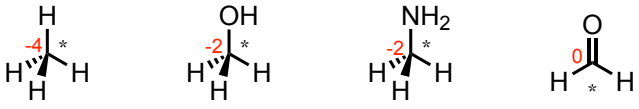
2-h. 4 other resonance structures

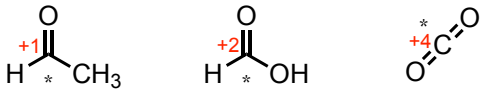


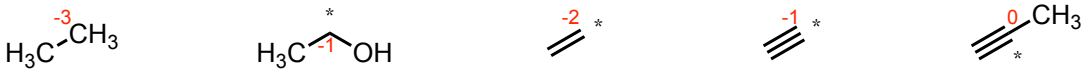
2-i. 2 other resonance structures

Skillbuilder Question 3: Oxidation States

Label the oxidation state of the indicated atoms in the molecules below.



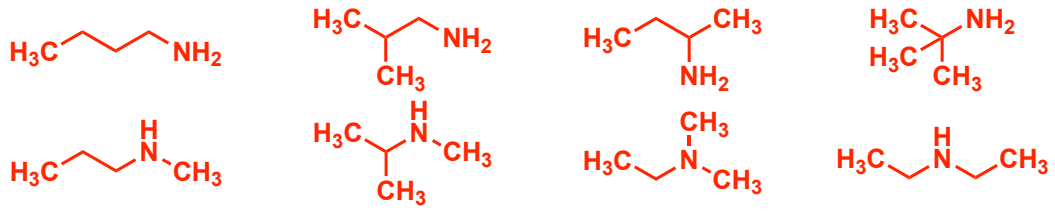




Skillbuilder Problem 5: Isomers

For each of the following formulae, determine the degrees of unsaturation and then draw line/skeletal structures of all possible structural/constitutional isomers (do not include stereoisomers). The number of possible structural isomers is provided to help guide your efforts.

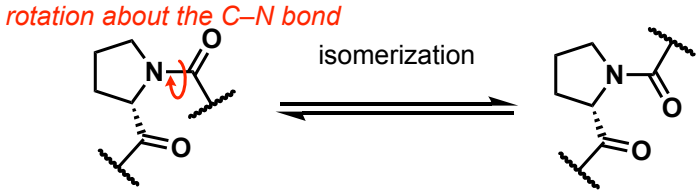
$C_4H_{11}N$ (8 structural isomers)



Challenge Problems

Challenge problems represent a higher level of difficulty than skillbuilder problems, typical of that found on midterm exams. You may need to integrate several concepts and apply them in order to answer the question.

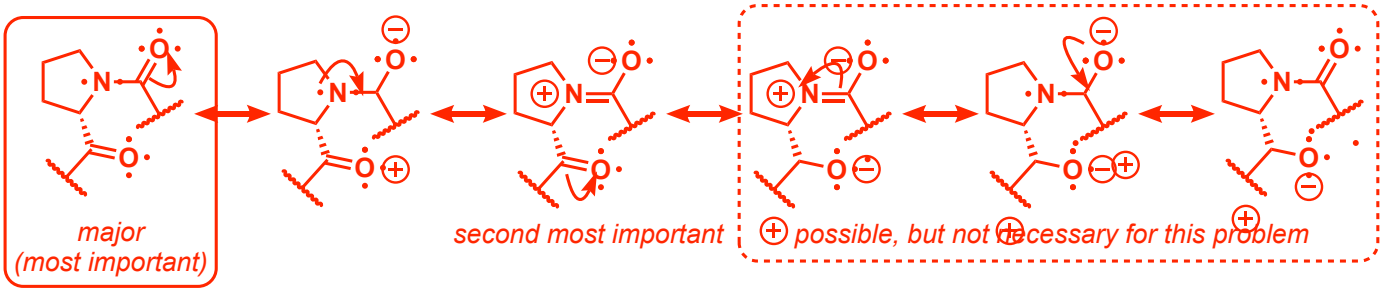
Challenge Problem 1: Prolinamide isomerization is often a rate-limiting step in protein folding. We will soon use molecular orbital theory to understand why it is a relatively slow isomerization, but for now, let's concern ourselves with the structural characteristics of the prolinamide isomers.



1-a. What kind of isomers are these prolinamide units? Justify your answer.

These prolinamide units are conformational isomers. They can be interconverted by rotation about the C–N single bond, as shown on the diagram above.

1-b. Provide all reasonable resonance structures of the prolinamide unit (either isomer). Use the **arrow-pushing formalism** to represent how the electron distribution changes between each resonance structure. Draw all lone pairs, and indicate formal charges where relevant. Circle the major resonance contributor and briefly justify your choice.

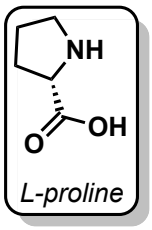


The major resonance contributor has a full octet on all atoms and no separation of charge; this makes it energetically better than the second most important resonance contributor which has separation of charge with a full octet on all atoms. All other resonance contributors are very minor as they do not have a full octet on all atoms.

1-c. You have probably realized (even if you don't yet know why) that rotation around a single bond is generally very easy while rotation around a double bond is much harder. Based on your answer in part **b**, can you speculate why prolinamide isomerization is relatively slow compared to other types of bond rotations that are involved in protein folding?

*In the second-most important resonance structure in part **b**, the C–N bond (around which rotation must occur) is a double bond. This means that the prolinamide fragment actually has some double bond character, rendering rotation around that bond harder/slower than rotation around a true single bond (as is the case from the other types of bond rotations involved in protein folding).*

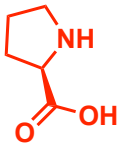
1-d. The prolinamide units above are derived from the free amino acid, L-proline. There are also several isomers of L-proline that we have not yet discussed. Determine the degrees of unsaturation of L-proline; then, draw and label one configurational isomer and three structural isomers of L-proline.



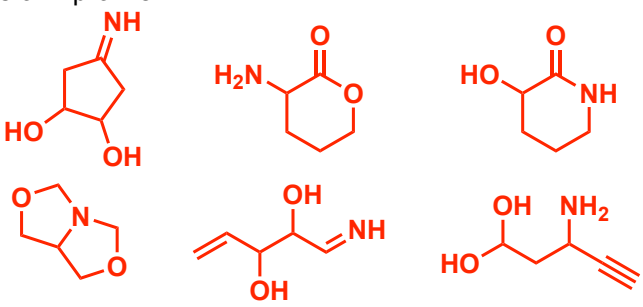
L-proline

1 ring + 1 double bond = 2 degrees of unsaturation

Molecular Formula: $C_5H_9NO_2$



Configurational Isomer

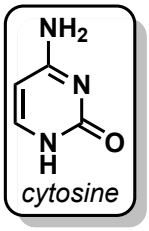


Structural Isomers

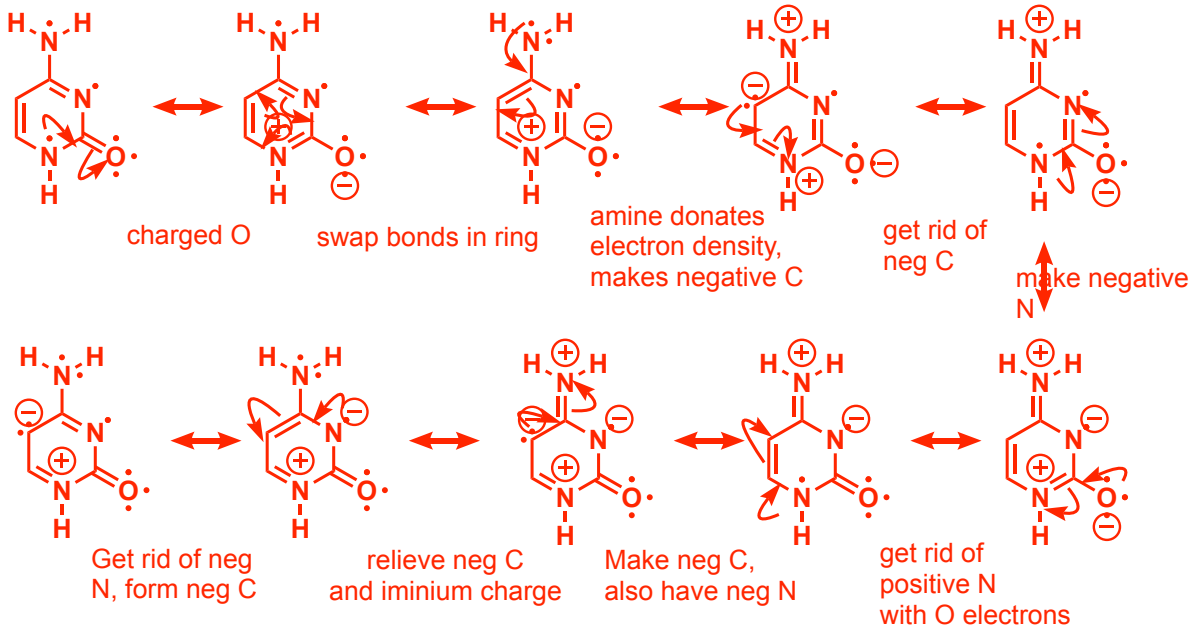
(There are many possible correct answers, only a few of which are shown here.)

Challenge Problem 2: Cytosine, shown below, is a component of RNA and DNA.

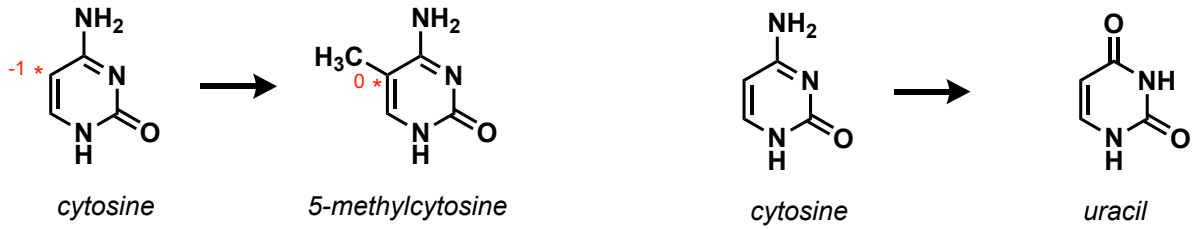
2-a. Provide all reasonable resonance structures for cytosine. Use the **arrow-pushing formalism** to represent how the electron distribution changes between each resonance structure. Draw all lone pairs, and indicate formal charges where relevant.



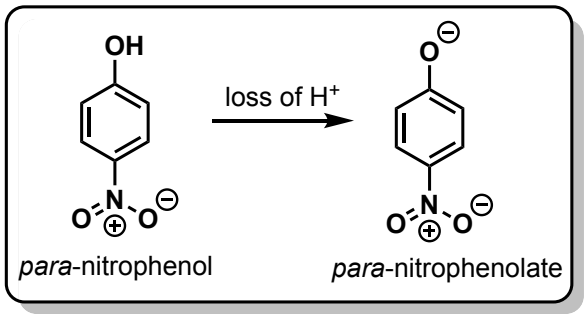
cytosine

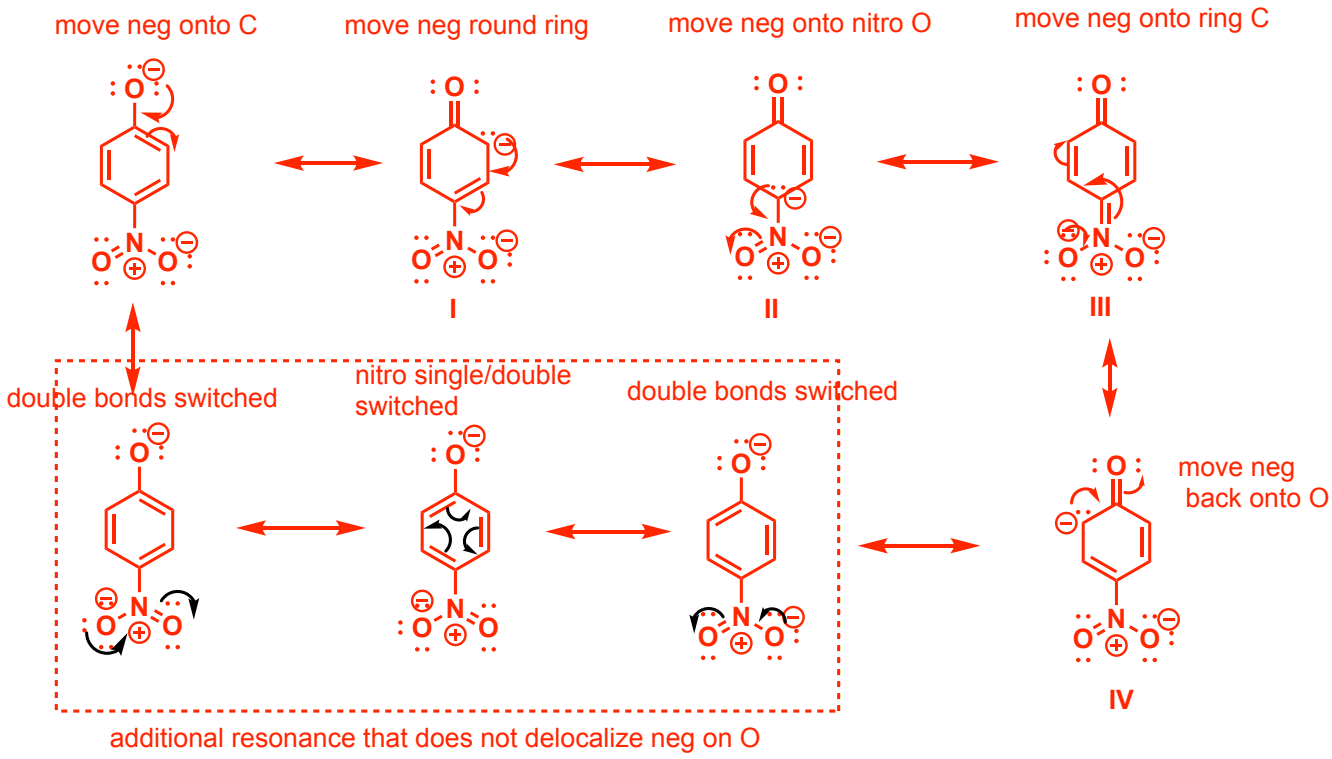


2-b. Cytosine can be transformed into several other molecules. For example, it can be methylated to 5-methylcytosine by DNA methyltransferase. It can also undergo deamination to form uracil. These two transformations are shown below. For each reaction, identify which carbon atoms, if any, undergo a change in oxidation state. Indicate whether the reactions are oxidations, reductions, or redox neutral processes.



3-a. Draw 4 reasonable resonance structures that show the delocalization of the new negative charge in *para*-nitrophenolate (not including the initial structure) and show how you convert between resonance structures using arrows. Draw all lone pairs and indicate charges where relevant. (Note: there are other resonance structures that do not involve this negative charge which you do not have to draw).





3-b. From the 4 structures you have drawn, identify which is the major contributor to the overall electronic distribution in the molecule.

structure III is the major contributor to overall electronic distribution (along with the initial structure) as the negative charge is on the more electronegative atom O, rather than on C as is the case in structures I, II and IV.